XIII. "Researches on the Phosphorus-Bases."—No. IX. Phospharsonium Compounds. By A. W. Hofmann, LL.D., F.R.S. Received July 24, 1860.

The facility with which the bromide of bromethyl-triethylphosphonium furnishes, when submitted to the action of ammonia and monamines, the extensive and well-defined group of phosphammonium-compounds, induced me to try whether similar diatomic bases containing phosphorus and arsenic might be formed by the mutual reaction between the bromethylated bromide and monarsines. There was no necessity for entering into a detailed examination of this class of compounds. I have, in fact, been satisfied to establish by a few characteristic numbers the existence of the phospharsonium-group.

## Action of Triethylarsine on Bromide of Bromethyl-triethylphosphonium.

On digesting the two substances in sealed tubes at 100°, the usual phenomena are observed; the reaction being complete after the lapse of twenty-four hours. The saline mass which is formed yields with oxide of silver in the *cold*, a powerfully alkaline solution, containing the hydrated oxide of ethylene-hexethylphospharsonium,

$$C_{14} H_{36} P As O_2 = \frac{[(C_2 H_4)''(C_2 H_5)_6 P As]''}{H_2} O_2.$$

It is thus obvious that the arsenic-base imitates triethylphosphine in its deportment with the brominated bromide. The two substances simply combine to form the dibromide of the phospharsonium,

$$[(C_{2} H_{4} Br)(C_{2} H_{5})_{3} P] Br + (C_{2} H_{5})_{3} As = [(C_{2} H_{4})'' \frac{(C_{2} H_{5})_{3} P}{(C_{2} H_{5})_{3} As}]'' Br_{2}.$$

The alkaline solution of the oxide of the phospharsonium exhibits the leading characters of this class of bases; I may therefore refer to the account which I have given of the oxide of diphosphonium. The saline compounds likewise resemble those of the diphosphonium. The dichloride and the di-iodide were obtained in beautiful crystalline needles, exhibiting a marked tendency to form splendidly crystallized double compounds. I have prepared the compounds of the dichloride with chloride of tin, bromide of zinc, trichloride of gold, and

lastly with dichloride of platinum. The latter compound was analysed in order to fix the composition of the series.

Platinum-salt.—The product of the reaction of triethylarsine upon the bromethylated bromide was treated with oxide of silver in the cold, and the alkaline solution thus obtained, saturated with hydrochloric acid and precipitated with dichloride of platinum. An exceedingly pale-yellow, apparently amorphous precipitate of diphosphonic appearance was thrown down, almost insoluble in water, but dissolving in boiling concentrated hydrochloric acid. The hydrochloric solution deposited, on cooling, beautiful orange-red crystals, resembling those of the diphosphonium-platinum-salt. The crystals, according to the measurement of Quintino Sella, belong to the trimetric system. The analysis of the platinum-salt led to the formula

$$\mathbf{C}_{14}\,\mathbf{H}_{34}\,\mathbf{P}\,\mathbf{As}\,\mathbf{Pt}_{2}\,\mathbf{Cl}_{6} \!=\! \left[ \, (\mathbf{C}_{2}\,\mathbf{H}_{4})^{\prime\prime}\,\frac{(\mathbf{C}_{2}\,\mathbf{H}_{5})_{3}\,\mathbf{P}}{(\mathbf{C}_{2}\,\mathbf{H}_{5})_{3}\,\mathbf{As}} \right]^{\prime\prime}\!\mathbf{Cl}_{2}\!,\,2\,\mathbf{Pt}\,\mathbf{Cl}_{2}\!.$$

The phospharsonium-compounds, and more especially the hydrated oxide of the series, are far less stable than the corresponding terms of the diphosphonium- and even of the phospharmonium-series. If the product of the action of triethylarsine upon the brominated bromide be boiled with oxide of silver instead of being treated in the cold, not a trace of the phospharsonium-compound is obtained. The caustic solution which is formed, when saturated with hydrochloric acid and precipitated with dichloride of platinum, furnishes only the rather soluble octahedral crystals of the oxethylated triethylphosphonium-platinum-salt\*. The nature of this transformation is clearly exhibited when a solution of the dioxide of phospharsonium is submitted to ebullition. Immediately the clear solution is rendered turbid from separated triethylarsine, which becomes perceptible, moreover, by its powerful odour, the liquid then containing the oxide of the oxethylated triethylphosphonium,

<sup>\*</sup> See the following Abstract.